NOVI TRENDOVI I TEHNIČKA REŠENJA

NEW TRENDS AND TECHNICAL SOLUTIONS

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The quote of Winston Churchill, the start of the end of the beginning, can be used to describe the situation after the news on October 5th broke out announcing that The European Parliament and the Counsil had reached a provisional deal which included specific bans on the use of various fluorinated compounds and a complete phase out by 2050. The writing on the wall is a wakeup call for those that have not yet understood that the end is nearer than what meets the eye. Although the announcement was provisional it still reveals what can be expected in the future.

The news must have been a bitter pill to swallow for those who have not started looking in to fluor free alternatives in due time and now have to hast through what others already have done and ready to take the markets.

For the environment the ban means a doublet fold reduction on the CO_2 emissions:

During the manufacturing of the fluorinated refrigerants the emissions of CO_2 equivalents are about 3-4 times higher than for some natural refrigerants and for the new series marketed as HFO it can amount more than 10 times the CO2 emissions producing naturally occurring working fluids.

In many cases refrigeration, air conditioning and heat pump systems with naturally occurring working fluids are about 10 to 15% more energy efficient than systems based on fluorinated fluids.

The big questions for many companies is what and how do we can handle the flammability of HC and other challenges that comes with naturally occurring working fluids? This is what this paper will dive more in to and give some answers to the issues that need to be considered.

1 Introduction

Putting limits on a popular group of refrigerants always creates some turbulence. A lot of arguments for and against surface and some can be valid while others can be characterized as slightly misleading – at best. Some are confused about what it take to move from the technology of yesterday to the technology of tomorrow.

The good news is that the thermodynamic rules of law still apply. Many have tried to work with R-32 in the past. This substance is slightly flammable and special care need to be taken to avoid a situation. Under the fire protection rules any substance which is flammable has to be treated as such, there is not such a thing a slightly flammable or similar nominations as found in ISO 817 class A2L or B2L. Flammables have to be treated with respect for the properties they have.

It is important to bear in mind that the fluids in many cases are tested under conditions at which they are not flammable but they can very easily be flammable under other conditions. That goes for both R-22 and R-134a but also others my have same properties. It is also important to bear in mind that it is the pure refrigerant which is tested, but in the systems there are very often oil and in some cases even also some water. It is a variable that has been discussed in many scientific papers over the years.

The same precautions apply to propane and all other hydrocarbons. Another piece of good news is that with good ventilation around you propane, and other flammable substances, are pretty difficult to ignite. All flammable gases have a lower flammability limit (LFL) and a upper flammability limit (UFL). These values, however, depend on pressure and temperature, so it is not a fixed value which makes it a little tricky. There is also a autoignition temperature (AIT) which is also a moving variable. This can be see from Figure 1. The main takeaway from this is that if you stay well below any concentration that can ignite, then you are on the safe side.

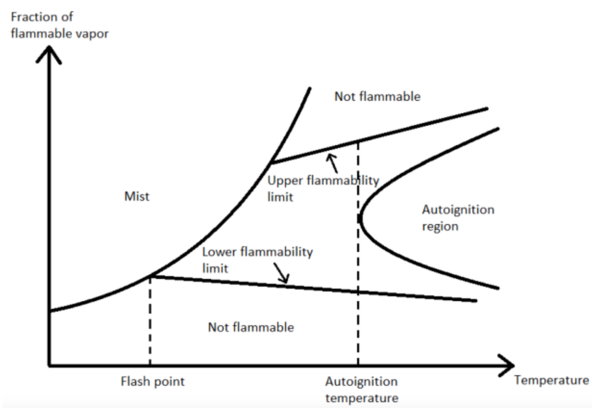

Figure 1 Different regions for flammability of gases. The curves are specific for the individual gas [1]

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The question then becomes how to ensure that we stay in the non-flammable area as shown in Figure 1. Following standard EN 378 part 3 §5.14 Machinery rooms for groups A2L, A2, A3, B2l, B2 and B3 refrigerants. Clause 5.14.1 says that the machinery room for systems using the mentioned safety classes of refrigerants shall be assessed with regard to flammability and classification according to the requirements of EN 60079-10-1 for the hazardous zone.

The European COMMISSION DIRECTIVE (EU) 2016/2037 of 21 November 2016 amending Council Directive 75/324/EEC as regards the maximum allowable pressure of aerosol dispensers and to adapt its labelling provisions to Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures

Table 1 The definition of flammable aerosol. The directives distinguish between flammable and non-flammable only. The lower flammability seen in ISO 817 is not used but as shown here it related to the pressure at 50°C

The pressure at 50 °C in the aerosol dispenser must not exceed the values provided for in the following table, depending upon the content of gases in the aerosol dispenser:

Content of gases	Pressure at 50 °C
Liquefied gas or mixture of gases having a flammable range with air at 20 °C and a standard pressure of 1,013 bar	12 bar
Liquefied gas or mixture of gases not having a flammable range with air at 20 °C and a standard pressure of 1,013 bar	13,2 bar
Compressed gases or gases dissolved under pressure not having a flammable range with air at 20 °C and a standard pressure of 1,013 bar	15 bar'

This definition gives much more sense than found in the current definition in ISO 817. This definition can easily be extended to all types of systems and working fluids and will be realistic to everyday life situations.

Emergency exhaust ventilation can be calculated by looking at EN 378 part 3 §6.3.3.1 it can be calculated by either dilution transfer openings and natural convection (§6.3.1) or by mechanical airflow (§6.3.3). The most common way is to ventilate with mechanical ventilation. The mechanical ventilation airflow must at least give the airflow calculated by:

$$m = \frac{10 \times V}{Q} \times \ln\left(1 - \frac{Q \times RCL}{10}\right)$$

And

$$Q = \frac{10}{RCL}$$

Where:

m – is the refrigerant charge in kg
V – is the room volume expressed in m^3
10 – is the expected maximum leak rate in kg/h
Q – is the ventilation airflow in m^3/h
RCL – is the refrigerant concentration limit in kg/m^3. ISO 817 earlier versions it was given in ppm, but in future editions it can be expected to appear in kg/m^3 as well.
ln – is the natural logarithm

The lower and simplified formula will give a higher ventilation rate than the first formula. The air extracted from the machinery room has to be blown out to a safe area and the size of the of this area is again defined in EN 60079-10-1.

The RCL in 817 is actually given in ppm, but in the standard there is a way to calculate the ppm values in to g/m^3. In coming versions of the standard this issue will be fixed making it easier to calculate the ventilation as given above.

It is worth noting that while LFL/LEL are often given the Auto Ignition Temperature (AIT) is not that often given. I EN 378 or ISO 5149 it says that the AIT must always be at least 100 K higher than the warmest part of the of the system. As can be seen in Figure 1 this is, like it also the case for LFL, not a constant value. In refrigeration and AC systems that is not so difficult to achieve the 100 K difference, but in high temperature heat pumps it can become a challenge.

When it comes to the purity of working fluids the reference is AHRI Standard 700 [2], which is freely available on the internet, is recommended as reference for the sourcing responsible. With this standard, any misunderstanding of what is purchased can be avoided. Ammonia is interestingly not included in the standard. He you might have to refer to guidelines from organisations, such as ASHRAE, see below, dealing with this topic.

ASHRAE Position Document on AMMONIA AS A REFRIGERANT says: "Refrigeration grade ammonia is 99.98 percent pure and is relatively free of water and other impurities (maximum: 150 ppm water, 3 ppm oil, 0.2 ml/g non-condensable). It is readily available inexpensive, operates at pressures comparable with other refrigerants and is capable of absorbing large amounts of heat when it evaporates."

2 Selecting the system layout

Selecting the system layout is also about selecting the working fluid, often referred to as the refrigerant. However, the most pressing challenge is the type of equipment because the lubricants can be a barrier to achieving higher temperatures much higher than about 160 °C. To make lubricants (often referred to as oil) traditionally were based on mineral oils. Some newer types of lubricants are the synthetic type with no carbon atoms, which forms soot at about 180 °C and coke about 200 °C. To make the lubricants more heat resistant the manufacturers often ad fluorine compounds which can form per- and polyfluoroalkyl substances (PFAS).

The solution to the lubricant problem is oil free systems, which can be found in some types of compressors. Another topic is the sealing materials. Here we have the same issue with synthetic sealing materials also containing PFAS potentials after end of use. To the non-moving seals other solutions are available but for valves with moving parts other materials need to be identified.

From compressed air screw compressors working oil free it is known that with surface treatment the compressors can run oil free with a maximum temperature slightly over 200 °C. This solution would allow compressors using e.g. systems with iso-Pentane of Hexane produce water or steam at about 160 to 180 °C. Only challenge could be that the surface treatment sometimes is done using fluorine compounds that could produce PFAS. With proper disposal, this challenge should be manageable in a safe manner. Other oil free compressors, use an external gear to keep a minimal clearance between the rotors, but the gear is lubricated, but the lubricant is out in the gas stream. By injecting liquid working fluid into the compressor through economiser ports, making the compressor partly flooded can close the gaps between the grooves and increase efficiency. A little liquid refrigerant will leave the compressor with the gas and will have to be dealt with.

In his paper, Ahrens, M.U. et al, 2022 [3], Marcel Ulrich Ahrens show how a twin screw can be used for producing temperatures up to between 175 and 210 °C in a hybrid cycle also referred to as the August Osenbrück's cycle, in recognition of the inventor of the cycle in 1895-1905.

Fritz Egger in his Patent application published March 17, 1994, DE 42 30 818 A1, shows different ways to apply the hybrid system. The drawings show a compressor apparently using an economiser port, so we can assume a type of screw compressor, since Vorhees compressor were not commonly used in this process.

The highest discharge temperatures was achieved with pure ammonia. The control is very delicate because when the liquid injection stops the remaining liquid evaporates and temperature increases rapidly. Once all the liquid is evaporated there will be no sealing between the lobes and there will be a backflow internally in the compressor causing the temperature rising, but pressure will not increase because gas pressure will go to the condenser.

Margaret M. Mathison et al. [4], show how a multi-compression in a scroll compressor can reduce the discharge temperature of the compression by injecting refrigerant through three ports. This can be done either from one level to the all ports or from different levels to the three ports. The refrigerant in this case is R-410 but it can apply to any cycle with sufficient pressure available. In this case it is scroll compressors that has been in the scope of the research project, however the same could possibly be introduced in screw compressors as well.

The ammonia/water hybrid system is one way to go. It is not the most common way chosen by the market. It is more common to use compression cycle, also referred to as the Carnot cycle. A number of fluids have been entering the market as shown by e.g. Cordin Arpagaus et al. [5]

Table 2 Published data from MAN Energy Solutions for the system in Esbjerg, Denmark (company home page) [6]

Performance table for two heat pump units	Winter	Summer
Heat sink		
Duty (MW_{th})	61	65
Supply temperature (°C)	70	70
Return temperature (°C)	33	37
Flow (kg/s)	400	516
Heat source		
Inlet temperature (°C)	4	14
Flow (kg/s)	4,000	4,000
Electrical input		
MW_{el}	18.4	17.4
COP	3.3	3.7
Power balancing capacity		
MW_e/30 sec	12.1	12.1

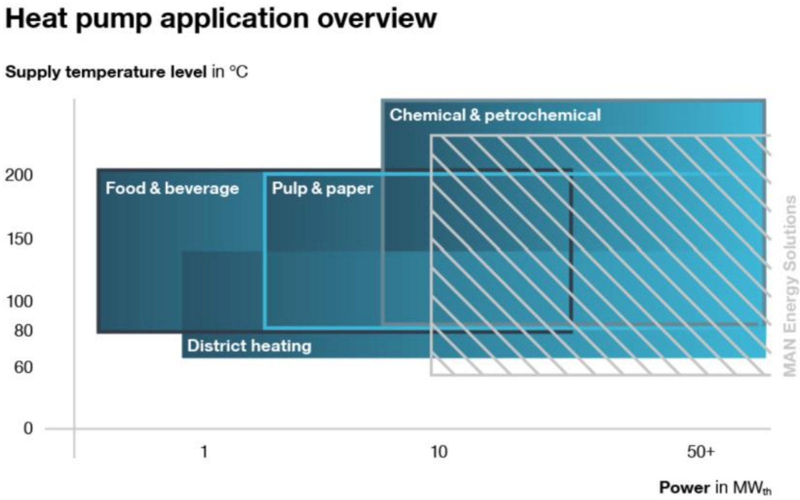
Most notably carbon dioxide (CO_2) is emerging in the many larger heat pump systems. The latest entry in this market is the very large heat pumps delivered by MAN Energy Solutions in Esbjerg, Denmark. The heat pumps are to deliver about 60 MW heating. The large motors, will also be part of the balancing market of the electric grid with a 30 seconds reaction time.

Most recently MAN Energy Solutions has signed another large order for a project in Aalborg, Denmark, with a heating capacity of 132 MW provided by three 44 MW heat pump units. The refrigerant used in both cases is CO_2.

CO_2 is one of the few non-flammable natural refrigerants. The other being water. MAN Energy Solutions on their homepage claim to be able to deliver 280 °C [7] steam to the customer.

Even being non-flammable CO_2 has to be taken seriously in case of a leak because of its ability to deplete oxygen. It is therefore recommended to have a personal detection system on you at all times in the machinery room and places where CO_2 can enter in case of major leak. Systems of the magnitude discussed here hold a relatively high amount of CO_2.

The markets served and the capacities are shown below



Also the hydrocarbons are seeing a renaissance after many years mostly being used in the petrochemical industry where staff know how to handle these substances in a safe manner. The flammability of the hydrocarbons is natural in these environments and procedures ensure the safety of establishment and staff. It is relatively rare to hear about accidents from these industries.

In modern time we now see hydrocarbons being used in domestic fridges and freezers. Also chillers are now becoming a more common product.

The domestic fridges are normally charged with iso-butane (R-600a) and the larger chillers and heat pumps are charged with propane (R-290). For low temperatures you find propene (R-1270) and for very low temperatures ethane (R-170) or even lower temperatures ethene (R-1150).

As noted before the hydrocarbon refrigerants are flammable, but they are not explosive which is often claimed by less educated persons. Ethane is a bit different from propane. Propane has a flame propagation around 40 cm/s where ethane has a flame propagation around 103 cm/s. With the high flame propagation comes the ability to create a higher pressure in closed environment. In average detonation velocity of dynamite is in range of 6000 m/s – far more than any refrigerant can do.

For safety reasons it should always be remembered that the hydrocarbons and their fluorinated cousins are heavier than air. Only ammonia vapor at room temperature is lighter than air – that being said, a fog of ammonia, which is a two phase phenomenon is heavier than air. All gases can form fogs when released and the content of oxygen in these fogs is extremely low – low enough to kill a human being in a matter of seconds. It is therefore important to take you safety precautions before getting near such a situation. Ventilation to disperse the fog is the best way to deal with the fog.

Other challenges is the proposed regulation of Per- and Polyfluoroalkyl Substances (PFAS) and Trifluoroacetic Acid (TFA). These substances are often referred to as “forever chemicals” because they have no know break down paths in nature. Since 2011 several papers have been published showing that the substances have an impact on the health of humans and species in nature. Therefore 5 countries have submitted a proposal for regulation of these substances at the European Chemical Agency (ECHA). There more than 10,000 substances in the market making it a task to go through all and evaluate all of them. The low hanging fruit seems to be the fluorinated hydrocarbons (HFC including the so called HFO, also being HFC’s) used as refrigerants. They are among the biggest part of the consumption and there are alternatives already being used.

3 Conclusions

With legislation in Europe and the United States of America pushing for a low Global Warming Impact (GWP) and zero Ozone Depleting Potential (ODP) of the refrigerants being used, the market will be forced to work more with gases that are flammable or oxygen depleting. It is therefore important to follow standards and guidelines published by IIF/IIR, IoR; IIAR, AIRAH and many others.

It is important as well that the staff are competent following the standard ISO 22712, previously known as EN 13313, because by training and education it is possible to make the staff aware of the risks and consequences if they don't follow the standards.

For many years chlorinated and fluorinated gases have been called "Safety Refrigerants". Using current standards the fluids were found not flammable, but a non-normative note in ISO 817 say that the refrigerants apparently not flammable as tested might be flammable under other conditions which we now know is true. Also the A2L class refrigerants are flammable and as shown the flammability levels may change at different temperatures and pressures. Also the Auto Ignition Temperature (AIT) is a moving target and depends on a number of parameters such humidity of the air and if there is lubricant/oil in the gas. This can also affect the pressure developed during the ignition.

The future systems are being developed as these words are being typed. Higher and lower temperatures with systems based on natural refrigerants. The requirements from users for phasing out sealing materials and lubricants containing components which can react and produce TFA or other PFAS substances is another challenge which will hit the industry regardless the working fluid used.

Be ready for all the changes that will challenge the industry in the years to come.

4 References

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